The Long-Term Testing of ZSM-5-Type Zeolite Containing Strontium for the High-Temperature Conversion of Methanol to Olefin

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Synopsis. Using ZSM-5-type zeolites containing alkaline earth metals (Mg, Ca, Sr), long-term tests for methanol conversion were carried out for up to 1000 h at 550 °C under a methanol LHSV of 2.3 h^{-1}. Strontium-containing zeolite showed the most stable activity. This was attributed to the effect of strontium on the acidity of the zeolite.

ZSM-5-type zeolites are excellent for the conversion of methanol to light olefins and gasoline.[1-7] It is well-known that a high selectivity to light olefins has been attained at high temperatures over highly siliceous zeolites.[8,9] However, catalyst deactivation is a serious problem under high reaction temperatures. The deactivation occurs predominantly for two causes; one is the poisoning of active sites due to the accumulation of carbonaceous deposits, and the other is the structure degradation of the zeolites by dealumination from the framework. In the former case, the deactivated catalyst can be regenerated by burning off the carbonaceous deposits, while in the latter case a practical method for regeneration has not yet been established. The deactivation due to the dealumination is, therefore, more serious than the coke deposition. Furthermore, it is known that the dealumination is accelerated in a moisture-rich atmosphere such as methanol conversion. In order to improve the catalyst life under high temperatures, the resistance against steaming must be much improved.

Recently, we reported that the ZSM-5-type zeolites containing alkaline earth metals (AE-ZSM-5, AE= Mg, Ca, Sr) showed an increased selectivity to olefins at temperatures above 500 °C.[10-12] Hence, we carried out a long-term life test of AE-ZSM-5, and compared the results of Sr-ZSM-5 with those of Mg-ZSM-5 and Ca-ZSM-5.

Experimental

The protonated zeolite catalysts (AE-ZSM-5, AE= Mg, Ca, Sr) with a SiO_2/Al_2O_3 ratio of 200 were prepared by the method described in our previous papers.[10,12]

Methanol-conversion runs were carried out under atmospheric pressure over a fixed bed in a quartz tube reactor (10 mm i.d.), and the product gas was analyzed by the use of TCD- and FID-type Yanaco AG-1000TFH auto gas chromatographs.[10] The reactant gas consisted of methanol/argon (1/1 mol/mol), while the argon served as a diluent as well as an internal standard for analysis. The products obtained will be abbreviated in the present paper as follows: ethylene=$C_2^=$; propylene=$C_3^=$;C_4-olefins=$C_4^=$; C_5-olefins=$C_5^=$; dimethyl ether=DME.

The catalyst regeneration was performed by burning off carbonaceous deposits under a stream of air/argon (0.8/1.0 v/v), just after DME appeared in the products. The temperature was maintained at 400 °C for the first 2 h, then raised to 550 °C, and finally maintained at 550 °C for 2 h.

The elemental composition, the ^{27}Al-MAS NMR spectra, and the diffuse reflectance FT-IR spectra of the hydroxyl groups of the zeolites were measured according to the methods described in our previous papers.[10,12]

Results and Discussion.

A long-term life test for the methanol conversion was carried out at a temperature of 550 °C and at a methanol LHSV value of 2.3 h^{-1}. For Sr-ZSM-5, a long-term life test was carried out for 1000 h, as is shown in Fig. 1. The catalyst was regenerated 12 times with intervals of from 74 to 79 h, while the methanol conversion was kept nearly constant (ca. 100%). The total yield of $C_2^=$ to $C_5^=$, the maximum value of which was 80 to 83%, decreased with time on-stream, but it was almost completely recovered by regeneration. Thus, the Sr-ZSM-5 catalyst was found to be stable and

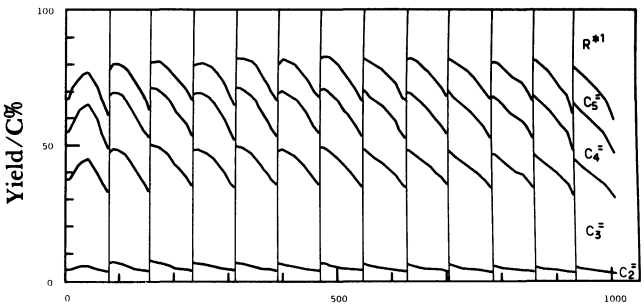

Fig. 1. Long-term life test over Sr-ZSM-5.
Reaction conditions: MeOH LHSV=2.3 h^{-1}, MeOH/Ar=1/1 mol/mol, temp=550 °C. *1) R is composed of paraffins, C_6^+-olefins, benzene, toluene, xylene, CO, and CO_2.

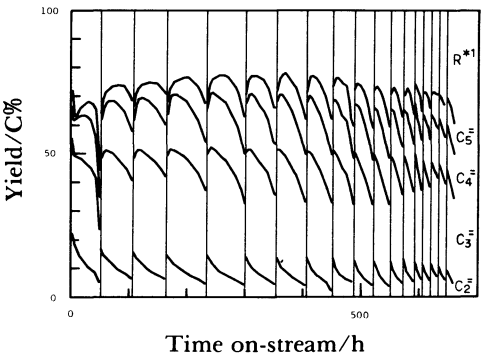

Fig. 2. Long-term life test over Mg-ZSM-5.
Reaction conditions: MeOH LHSV=2.3 h^{-1}, MeOH/Ar=1/1 mol/mol, temp=550 °C. *1) R is composed of paraffins, C_6^+-olefins, benzene, toluene, xylene, CO, and CO_2.

to show a high selectivity to light olefins.

On the other hand, for Mg-ZSM-5, a long-term life test was terminated at 660 h; the catalyst should be regenerated at shorter intervals because of the ease of deactivation, as is shown in Fig. 2. The maximum total yield of $C_2^=$ to $C_5^=$ during the regeneration interval ranged from 68 to 77% during the first 400 h time on-stream and decreased slightly after that. It is, therefore, concluded that the Mg-ZSM-5 catalyst is less stable and shows a lower selectivity to light olefins than that of Sr-ZSM-5.

For Ca-ZSM-5, a long-term life test was carried out for 1000 h, as is shown in Fig. 3. The total yield of $C_2^=$ to $C_5^=$ changed in a manner similar to that of Sr-ZSM-5. The number of regenerations, 10 times, was less than that of Sr-ZSM-5. The maximum total yield of $C_2^=$ to $C_5^=$ was 83 to 86%, higher than that of Sr-ZSM-5. However, the regeneration interval should be gradually shortened from 120 to 75 h along with the time on-stream. This implies that the active sites are rather unstable for Ca-ZSM-5 and that the life time for Ca-ZSM-5 is shorter than that of Sr-ZSM-5.

The three catalysts used in the long-term life tests were characterized by means of ^{27}Al-MAS NMR spectroscopy. The intensities of the peak at about 53 ppm assigned to tetrahedrally coordinated aluminium[13] were also measured. The intensity ratios, which means the percentage of a 53 ppm peak intensity of the used catalysts relative to that of the corresponding fresh catalysts, are listed in Table 1.

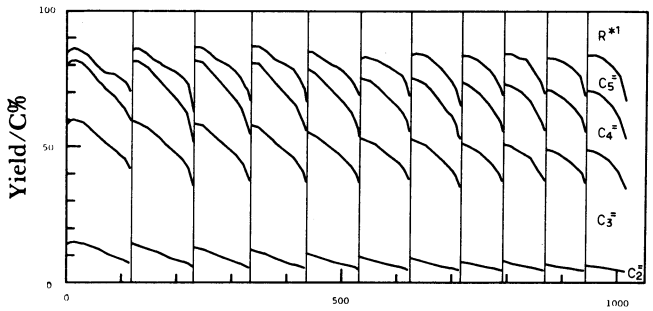

Fig. 3. Long-term life test over Ca-ZSM-5.
Reaction conditions: MeOH LHSV=2.3 h^{-1}, MeOH/Ar=1/1 mol/mol, temp=550 °C. *1) R is composed of paraffins, C_6^+-olefins, benzene, toluene, xylene, CO, and CO_2.

The ratio for Sr-ZSM-5 is 94%, distinctly higher than those of both Mg-ZSM-5 (18 to 19%) and Ca-ZSM-5 (32 to 56%). This implies that Sr-ZSM-5 has a higher resistance against the dealumination of the framework. It is considered that the acidity of zeolites originates from tetrahedrally coordinated aluminium, so that the long catalytic life of Sr-ZSM-5 (Fig. 1) is based on the greater resistance against the dealumination of the aluminosilicate framework.

Figure 4 shows the diffuse reflectance FT-IR spectra of hydroxyl groups for the three catalysts before and after the life tests. As has previously been reported,[14] each of the spectra is characterized by two well-defined peaks at 3605 and 3730—40 cm^{-1}. The low-frequency peak is assigned to an acidic bridged OH of Si(OH)Al, and the high-frequency one, to a terminal Si–OH or OH of the extra-framework silica. The broad peak near 3500 cm^{-1} is attributed to hydrogen bonding

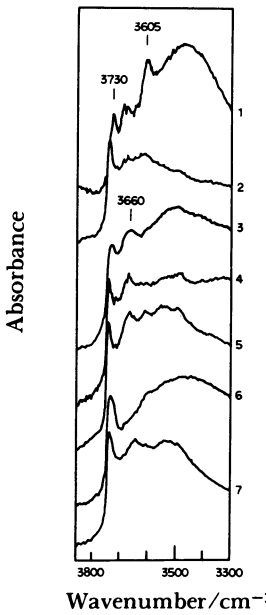

Fig. 4. IR spectra of AE-ZSM-5 before and after the life test.
1: Fresh Mg-ZSM-5. 2: Mg-ZSM-5 after the life test (660 h). 3: Fresh Ca-ZSM-5. 4: Upper-layer catalyst of Ca-ZSM-5 after the life test (1000 h). 5: Lower-layer catalyst of Ca-ZSM-5 after the life test (1000 h). 6: Fresh Sr-ZSM-5. 7: Sr-ZSM-5 after the life test (1000 h).

Table 1. Characteristics of AE-ZSM-5 before and after the Long-Term Life Test

Catalyst	Chemical composition[a] (Molar ratio)		Particle size (μm)	Relative intensity of the 53 ppm peak[b] after life test[c] (%)	
	SiO_2/Al_2O_3	AE/Al_2		Upper-layer[d]	Lower-layer[d]
Mg-ZSM-5	212	0.25	3—4	18	19
Ca-ZSM-5	200	2.63	4—6	32	56
Sr-ZSM-5	218	2.81	4—6	94	94

a) After proton ion-exchange. AE=Mg, Ca, and Sr. b) The intensity ratio (×100) of the 53 ppm peak of the used zeolite to the corresponding fresh one was determined by means of ^{27}Al-MAS NMR. c) The life tests were carried out at 550 °C under a MeOH LHSV of 2.3 h^{-1}, diluted with argon (MeOH/Ar=1/1 mol/mol). The total life times are 660 h for Mg-ZSM-5, 1000 h for Ca-ZSM-5 and 1000 h for Sr-ZSM-5. d) The upper-layer is 25% of the total volume of the catalyst, while the lower-layer is 75%.

between adjacent hydroxyl groups.[14] For Mg-ZSM-5, the peak at 3605 cm^{-1}, which was clearly observed in the fresh catalyst, disappeared nearly completely after the life test for 660 h, as is shown by Curves 1 and 2. This disappearance seems to be consistent with the release of a large number of aluminium atoms from the framework.

For the fresh Ca-ZSM-5 (Curve 3), the intensity of the peak at 3605 cm^{-1} was very low. We ourselves have previously reported[11] that the addition of calcium or strontium to the starting materials in the zeolite synthesis decreases the strong acid sites, corresponding to the peak at 3605 cm^{-1}, observed for the as-made zeolite catalyst because of the partial replacement of the H^+-acid sites for the calcium or strontium ions. On the other hand, the strong acid sites of the working catalyst gradually increase with the time on-stream in the methanol-conversion run because of the migration of the calcium ions from the initial sites. As compared to the 3605 cm^{-1} peak intensity of the fresh catalyst, that of the upper-layer catalyst of the reactor (Curve 4) remained almost unchanged, while that of the lower-layer one (Curve 5) increased. It is plausible that the deterioration of the catalyst, its dealumination, would take place in a greater degree at the upper-layer catalyst, since methanol was fed from the top of the reactor. The results for ^{27}Al-MAS NMR (Table 1) clearly support this possibility; that is to say, the relative intensity of the 53 ppm peak at the upper-layer catalyst (32%) is lower than that of the lower-layer one (56%). It is concluded, therefore, that the very low intensity for the upper-layer part is due to dealumination, while the increase in the intensity for the lower-layer part is due to the release of calcium ions from the strong acid sites, as has been mentioned above. This conclusion is also supported by the previous report that steam produced by methanol conversion accelerated the release of calcium ions from the acid sites.[15]

On the other hand, the peak at 3605 cm^{-1} was not observed for either the fresh Sr-ZSM-5 or the used one, as is shown by Curves 6 and 7. These observations of the FT-IR and ^{27}Al-MAS NMR spectra indicate that Sr-ZSM-5 is a remarkably stable catalyst for methanol conversion. From these results, it was confirmed that among AE-ZSM-5 Sr-ZSM-5 was the best catalyst in both the yield of light olefins and the catalyst life.

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